

# Oxidation behavior of rare earth oxide-coated Fe20Cr and Fe20Cr5Al alloys

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**Abstract** This article presents the influence of surface additions of nanocrystalline rare earth (RE) oxides CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> + La<sub>2</sub>O<sub>3</sub> on the isothermal oxidation behavior of Fe20Cr and Fe20Cr5Al at 1000 °C. Thermogravimetric studies revealed parabolic kinetics in all cases and the scale thickness on specimen surfaces varied with the nature of RE oxide. The oxidation resistance of specimens coated with two RE oxides was significantly higher than those coated with either one of the two oxides. The marked increase in the oxidation resistance of the alloys coated with two RE oxides is due to optimization of RE ion radius and RE oxide grain size/shape.

**Keywords** Iron-chromium alloy · Oxidation · Rare earth oxides

## Introduction

Reactive elements, especially rare earths (RE) have been used to improve high-temperature oxidation resistance of chromium dioxide and alumina forming alloys. The improvements are in the form of reduced oxidation rates and increased scale adhesion [1]. The RE can be added to the alloy as elements or as oxide to form dispersions. It can also be introduced into the surface by ion implantation or applied as an oxide coating to the surface of the alloy [2]. A variety of precursors have been used to obtain RE oxide

coatings on metallic surfaces. The use of sols, followed by its transformation to gel is referred to as the sol–gel technique and it produces oxide particles in the range 2 nm to 1 μm.

RE oxide sols have been applied to metallic substrates by a suitable technique to form a coating, followed by its transformation to a gel coating. Marked influence of surface deposited RE oxides on the isothermal [3] and cyclic [4] oxidation behavior of alumina and chromia forming alloys has been observed and reported. Certain RE oxides like La<sub>2</sub>O<sub>3</sub> and Pr<sub>2</sub>O<sub>3</sub> decreased the oxidation rates of chromia forming alloys more than other oxides like CeO<sub>2</sub> [4]. Nevertheless, increasing demand in recent years for even higher oxidation resistant chromia and alumina forming alloys has led to attempts at optimizing RE additions [5]. This article presents the effect of coatings of nanocrystalline oxide gels of CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub> + La<sub>2</sub>O<sub>3</sub> on the oxidation behavior of a Fe20Cr and a Fe20Cr5Al alloys. The mechanism by which these REs improved overall oxidation resistance of the alloys is also discussed.

## Methods and materials

Sols of La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, and CeO<sub>2</sub> + La<sub>2</sub>O<sub>3</sub> were prepared as aqueous dispersions with nitric acid and a non-ionic surfactant, heated to 80 °C for 1 h to form a sol, the RE oxide sol then sprayed on 2 × 2 × 3 mm specimens of the two alloys to form a coat and finally the specimens heated to 150 °C to form a 10 μm thick surface layer of RE oxide gel. These specimens were isothermally oxidized at 1000 °C for about 400 min in a thermogravimetric balance to obtain mass gain per unit area versus time curves. The specimen surfaces, prior to and after the oxidation tests,

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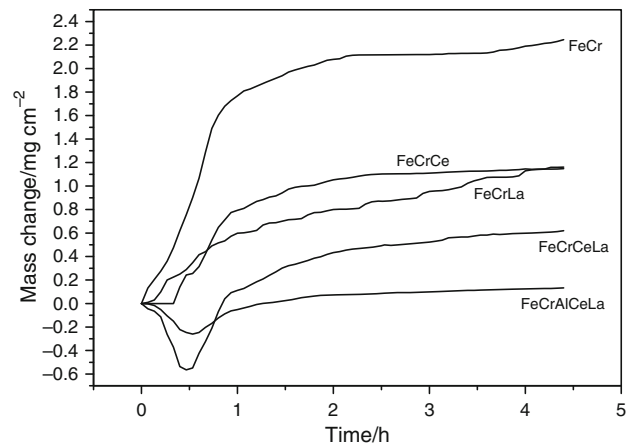
were examined in a scanning electron microscope (SEM) coupled to an energy dispersive spectroscopy (EDS) system.

## Results and discussion

Having observed in previous studies: (a) low cost with moderate influence of  $\text{CeO}_2$  on oxidation resistance of FeCr alloy; (b) marked influence of  $\text{La}_2\text{O}_3$  and  $\text{Pr}_2\text{O}_3$  on increasing oxidation resistance of FeCr alloy; (c) direct correlation between RE ion radius and oxidation resistance; (d) influence of RE oxide morphology; (e) varying coverage of the different RE oxides, attempts to optimize RE oxide use to increase oxidation resistance of chromia and alumina forming alloys was undertaken [4]. To this effect, evaluation of the effect of simultaneous addition of two RE oxides was the first step.

Scanning electron micrographs of  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  gels are shown in Fig. 1. Differences in morphology can be seen. The former consists of mainly cubes and the latter, a mix of cubes and rods.

The isothermal oxidation curves of uncoated Fe20Cr,  $\text{CeO}_2$ -coated Fe20Cr,  $\text{La}_2\text{O}_3$ -coated Fe20Cr,  $\text{CeO}_2 + \text{La}_2\text{O}_3$ -coated Fe20Cr, and  $\text{CeO}_2 + \text{La}_2\text{O}_3$ -coated Fe20Cr5Al specimens are shown in Fig. 2. The mass gains of the uncoated and RE oxide-coated Fe20Cr and Fe20Cr5Al specimens during oxidation are due to formation of  $\text{Cr}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , respectively on the specimen surfaces and these oxides did not spall [3, 4]. All the specimens revealed parabolic oxidation behavior. The effect of rare earth oxide addition to the surface of the Fe20Cr alloy was clearly evident upon comparison of the curves of Fe20Cr and RE oxide covered Fe20Cr specimens. Substitution of  $\text{CeO}_2$  with  $\text{La}_2\text{O}_3$  showed some improvement in oxidation behavior. However, when the two oxides  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  were jointly present on the surface, the improvement in oxidation resistance was significant. The curve of the Fe20Cr5Al specimen indicated even higher oxidation resistance. This could be attributed to the joint effect of the



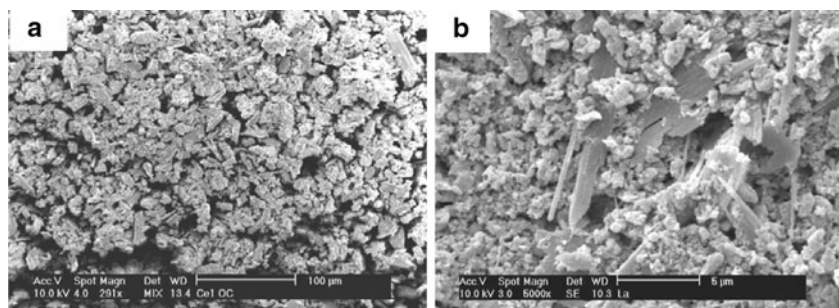
**Fig. 2** Isothermal oxidation curves of uncoated,  $\text{CeO}_2$ -coated,  $\text{La}_2\text{O}_3$ -coated, and  $\text{CeO}_2 + \text{La}_2\text{O}_3$ -coated Fe20Cr as well as  $\text{CeO}_2 + \text{La}_2\text{O}_3$ -coated Fe20Cr5Al at 1000 °C

low oxidation rate of alumina forming alloys and the effect of the rare earth ion on alumina formation.

## General discussion

Coverage of  $\text{CeO}_2$  and  $\text{La}_2\text{O}_3$  gels on metallic specimens is considered to be very good compared to the other RE oxides [4]. Marked variations in the extent to which different RE oxides affect oxidation rate of specially chromia forming alloys was reported elsewhere and direct correlations found between RE ion radius and oxidation resistance [4]. In the absence of RE, the new oxide scale grows at the oxide/oxygen interface and in the presence of RE it grows at the metal/oxide interface. The RE oxide coating on the alloy surface gets incorporated in the growing scale and the RE ions segregate to the grain boundaries in the scale [3]. The RE ions at the scale grain boundaries then diffuse through the oxide scale to the gas interface. Proof of this was shown after prolonged oxidations [6]. When the RE ion concentration at the grain boundaries in the scale reaches a critical amount, it results in two effects. The first

**Fig. 1** Scanning electron micrographs of  $\text{CeO}_2$  (a) and  $\text{La}_2\text{O}_3$  (b) gels



is inhibition of normal outward transport of alloy cations along the scale grain boundaries due to the slower diffusion of the large RE ions along the same grain boundaries. It is also probable that large RE ions diffuse slower than small RE ions. Consequently, large RE ions probably slow down alloy cation diffusion in the oxide scale even more than small RE ions, resulting in reduced scale growth [6, 7]. The second effect is reduction in scale grain growth and this is due to a solute-drag effect of the RE ions at the scale grain boundaries. This leads to smaller average grain size of  $\alpha$ -Cr<sub>2</sub>O<sub>3</sub> scales and higher scale plasticity. This mechanism is also valid for alumina scale forming alloys, but to a lesser extent.

There is evidence that RE containing spinels form in the growing scale, depleting the RE ion in the scale, necessary to block outward base metal ion diffusion to the oxide/oxygen interface. It is believed that in the presence of two different RE oxides, spinel formation, even if energetically favored at specific regions, would locally deplete just one of the two RE ions, leaving behind the other RE ion to hinder Cr or Al ion diffusion.

## Conclusions

1. The oxidation resistance of Fe20Cr-coated with CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> was higher than that of the same alloy coated with either RE oxide.

2. The Fe20Cr5Al alloy-coated with the two RE oxides revealed the highest oxidation resistance.

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